

REMARKS

Reconsideration and allowance of this application are respectfully requested.

All pending claims, 1-54, stand rejected for a single issue: obviousness. The applicants traverse. No prima facie obviousness is present on this record.

The primary issue is whether claims 1-15, 17-20, 22-27, 29-36, 38-40, 44-46, 48, 49, and 51-54 are unpatentable over Narang (USP 6,146,716) in view of Mirkin (USP 6,635,311).

The prosecution record to date provides a description of Narang and a description of Mirkin. However, the prosecution record to date provides no motivation to combine these references. Hence, the present obviousness rejections represent mere impermissible hindsight reconstruction of the invention, not prima facie obviousness.

In addition, the applicants respectfully submit that Narang relates to much larger scale lithography, e.g., microlithography and larger, than both the present claims and Mirkin. One of ordinary skill in the art knows that nanoscale miniaturization (e.g., moving from micro to nano) is generally more difficult than it may appear. One of ordinary skill in the art knows, for example, that microlithography and nanolithography are not interchangeable, and reference to one does not suggest the other. Rather, use of nanolithography requires a “paradigm shift” and “radically different” approaches. See Marc J. Madou, *Fundamentals of Microfabrication, The Science of Miniaturization*, 2nd Ed. 2002, pages 58-59 (copy attached). Another review reference states (copy attached):

The microelectronics industry, which took off in the 1960s, is already large, and the micromechanics industry began to grow exponentially in the 1990s. The micrometer arena still requires a great deal of basic and applied research. In the nanometer regime, a radically different approach to the production of objects is emerging...

See Direct-Write Technologies for Rapid Prototyping Applications, Sensors, Electronics, and Integrated Power Sources, Ed. A. Pique and D. B. Chrisey, pages 557-559, 2002.

Given the radical approaches needed for nanolithography, the applicants also stress that Narang does not describe any actual working examples. This reduces the motivation by one of ordinary skill in the art to turn to and actually rely on Narang to solve a problem in the real world related to nanolithography. In contrast, the applicants do describe working examples which can be useful in solving real problems, and the applicants invite the examiner to review the merits of the working examples in supporting the claims.

The Examiner also cites against selected claims U.S. Patent No. 6,271,130 to Rajh, which further supports the applicants' position and confirms no prima facie obviousness has been established in the record. Rajh directly teaches that "the available technology cannot easily establish dimensions for electronic components less than about 100 nm – 200 nm" (col. 1, lines 30-35).

Moreover, the record does not indicate any motivation to combine the first two references with Rajh. Rajh does not describe use of coated tips and provides a fundamentally different lithography approach. Hence, Rajh does not overcome any deficiencies by the Narang/Mirkin combination and appears to only be used as hindsight reconstruction of the invention.

Finally, the Examiner also cites to Peeters (USP 6,325,904) to establish obviousness of selected claims. Again, however, no motivation to combine is present in the record. Peeters would appear to have little to do with Narang or Mirkin. It relates only to protein detection, which is not relevant to Narang or Mirkin. Hence, Peeters also does not help

establish prima facie obviousness. The applicants note again that Peeters does not provide any working examples useful for solving real world problems.

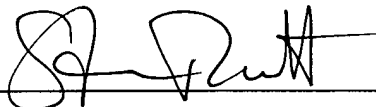
In conclusion, a Notice of Allowance is respectfully requested, and the Examiner is invited to contact the undersigned if any questions remain. The applicants ask that the Examiner review the patentability of each claim independently.

The applicants submit fees for a three month extension of time. The Commissioner is hereby authorized to charge any additional fees which may be required regarding this application under 37 CFR §§ 1.16-1.17, or any other section, or credit any overpayment, to Deposit Account No. 19-0741. Should no proper payment be enclosed herewith, as by a check being in the wrong amount, unsigned, post-dated, otherwise improper or informal or even entirely missing, the Commissioner is authorized to charge the unpaid amount to Deposit Account No. 19-0741.

Respectfully submitted,

Date February 11, 2005

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Fundamentals of
MICROFABRICATION
The Science of Miniaturization

Second Edition

Marc J. Madou



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Focused Ion Beam and Deep Ion-Beam Lithography

For ion-beam construction, liquid metal ion (LMI) sources are becoming the choice for producing high-current-density submicrometer ion beams. With an LMI source, liquid metal (typically gallium) migrates along a needle substrate. A jet-like protrusion of liquid metal forms at the source tip under influence of an electrical field. The gallium-gallium bonds are broken under the influence of the extraction field and are uniformly ionized without droplet or cluster formation. LMI sources hold extremely high brightness levels ($106 \text{ A/cm}^2 \text{ sr}$) and a very small energy spread, making them ideal for producing high-current-density submicrometer ion beams. Beam diameters of less than 50 nm and current densities up to 8 A/cm^2 are the norm. In addition to Ga, other pure element sources are available, such as indium and gold. By adopting alloy sources, the list expands to dopant materials such as boron, arsenic, phosphorus, silicon, and beryllium.

As in the case of e-beam systems, ion-beam lithography offers direct write and flood exposure fabrication opportunities. Compared to photons (x-rays and light) or electrons, ions chemically react with the substrate, allowing a greater variety of surface modifications such as patterned doping. The resolution of ion-beam lithography is better than for electrons, because the secondary electrons produced by an ion beam are of lower energy and have a short diffusion range so that hardly any backscattering occurs. The ion-beam spot size is the smallest possible—smaller than UV, x-ray, or electron-beam spots. The smallest focused ion beam (FIB) spot currently reached is about 8 nm, accomplished by using a two-lens microprobe system and a single-isotope gallium ion source. With this setup arrays of dots were produced in a 60 nm thick PMMA layer with dot dimensions ranging from 10 to 20 nm.¹⁰⁷ Ion-beam lithography experiences the same drawbacks as an electron-beam system in that it requires a serially scanned beam and a vacuum.

Focused ion beams can be used to perform maskless implantation and metal patterning with sub-micrometer dimensions. Focused ion beam also has been applied to milling in IC repair, maskless implantation, circuit fault isolation, and failure analysis (see Table 1.7). Some micromachining applications of ion-beam technology will be reviewed in Chapters 2 and 7. As a machining tool, FIB is very slow. Except for research, it may take a long time to become an accepted “micromachining tool.” For additional reading on ion-beam lithography in general refer to Selinger¹⁰⁸; for more specific reading on focused ion-beam-induced deposition, see Brodie.²⁸

Using high-energy (2 MeV) protons deep ion-beam lithography (DIBL) in PMMA produces submicron (300 nm) walls with an aspect ratio approaching 100. Three-dimensional complex microstructures with smooth walls and corners have been produced this way. The range of 2 MeV protons in PMMA is $63 \mu\text{m}$.¹⁰⁹ Multiple exposures at different ion energies (e.g., 0.6 and 2 MeV) allow production of multilayer structures in single layer resists such as SU-8.¹¹⁰

Ion Projection Lithography

Ion projection lithography (IPL) is another of the candidates for high-throughput lithography dedicated to future 50 nm and

sub-50-nm IC generations. Protons are generated by a radio frequency driven filament. Efforts are especially strong in Europe in this area (e.g., at IMS, <http://wwwold.ims-chips.de/>). The ion flood lithography mask typically consists of a silicon membrane a few microns thin ($3 \mu\text{m}$) with pattern openings that allow protons to pass through.¹¹¹ The mask fabrication process involves silicon-on-insulator (SOI) and dry etching.¹¹² Current IPL approaches, like SCALPEL, are $4\times$ technologies. Depth of focus is large and may reach up to $500 \mu\text{m}$. The optics in IPL are all electromagnetic, and the potential for a $50 \times 50 \text{ mm}$ exposure field exist.

Comparison of Ion-Beam Lithography with E-Beam Lithography

Ion-beam lithography has at least two advantages over electron-beam lithography: (1) it has almost two orders of magnitude higher resist sensitivity, and (2) it has negligible ion scattering in the resist and very low backscattering from the substrate. A major problem is the potential for damage to sensitive electronic functions from the high energy ions.

Emerging Lithography Technologies

Introduction

In this section, we cover the emerging fields of proximal probe lithography, very thin to monolayer lithography, soft lithography, and 3D lithographies including holographic lithography, stereolithography, and lithography on nonplanar substrates using high-precision linear and rotating positioning stages. These are more futuristic lithography methods, some of which could cause a paradigm shift in the improvement of CD printing capability by perhaps a factor of 100. These would enable devices that are a few nanometers in size and have switching speeds in the terahertz range. More details and additional references on the topics covered in this section can be found in the thorough review article by Xia et al.¹¹³

Scanning Probe Lithography

STM/AFM Background

The scanning tunneling microscope (STM) images the surface of conducting materials with atomic-scale detail. STM was invented by Gerd Binnig and Heinrich Rohrer of IBM's Zurich Laboratory in 1985 (they received the 1986 Nobel Prize for their invention).¹¹⁴ In general, STM works by bringing a small conducting probe tip up to a conducting surface. When the probe is very close to the surface (less than 10 \AA) and operating voltages in the $\pm 10\text{-V}$ range are applied, very small currents are produced, because the electrons in the probe and the surface have wave functions extending beyond the physical surface boundaries. To the extent that these spillover wave functions overlap, a measurable current results. The interesting part about this current is that it depends exponentially on the spacing between the two conductors (as well as the voltage). A piezoelectric transducer accomplishes the z-axis distance variation between tip and sam-

ple. By changing the distance over 1 Å, the current changes by a factor of ten. In practice, the current is kept constant through a feedback mechanism, and the probe moves up and down over the surface following the atomic contours it “sees.” The images produced by the STM come from the electronic structure as well as from the geometry of the sample. Up to 100 times more powerful than SEMs, scanning tunneling microscopes measure objects in the angstrom range. Over time, many proximal probe were developed, and STM belongs now to a large new family of very local, proximal probes, such as atomic force microscopes (AFMs), scanning electrochemical microscopes (SECMs), scanning thermal microscopes, scanning capacitance microscopes, magnetic force microscopes, scanning pH probes, etc., enabling microscopy of almost any type of material and property. The common feature of these instruments is that their resolution is not determined by visible light used for the interaction with the probed object, as in conventional microscopy.¹¹⁵

Scanning Probe Lithography

Introduction

Lithography utilizing electrons from a scanning probe offers several potential advantages over writing with a traditional e-beam source.¹¹⁵ One important benefit is that the low energy of electrons in SPL (<50 eV) as compared to those in EBL (300 eV to 100 keV) avoids the detrimental effects of electron back-scattering, thereby virtually eliminating proximity effects and thus producing enhanced resolution and superior pattern fidelity.¹¹⁶ Due to the small tip-to-sample distance, extremely small spot sizes are achievable so that the exposure dose may be confined to a beam diameter of less than 10 nm. The method enables a wider exposure latitude than EBL, a fact demonstrated in Figure 1.45.¹¹⁷ In this figure, line width is plotted vs. dose for SAL601 resist using both EBL and SPL lithography systems. From the lower slope of the SPL curve, one deduces that SPL has higher dose latitude than EBL—in other words, SPL is less

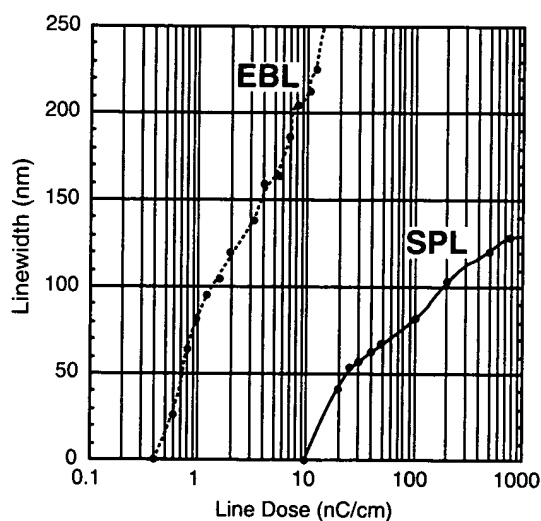


Figure 1.45 Line width vs. dose for SAL601 resist using both EBL and SPL lithography systems. (From K. Wilder et al., *J. Vac. Sci. Technol.*, B16, 3864–3873, 1998.¹¹⁷ Reprinted with permission.)

sensitive to dose variations. On the other hand, SPL is less sensitive and does require a higher dose to write the same feature size. The mechanism of electron bombardment in SPL is very different from that in EBL. In EBL, the mean free path of the bombarding electrons is long compared to the resist thickness. In contrast, low-energy electrons in SPL have a mean free path below 2 nm and reach through the resist under the influence of an electrical field, undergoing a number of scattering events before reaching the resist /substrate interface.¹¹⁷ The latter makes it clear why a thinner resist will result in a better expected resolution. The influence of secondary electrons (i.e., all electrons emanating from the resist/substrate) in proximal probe lithography was investigated recently by Völkel et al.¹¹⁸

Modes of Pattern Generation in Scanning Probe Lithography

The Naval Research Laboratory (NRL) worked with proximal probes to pattern thin films of chemically amplified negative e-beam resist (SAL-601 from Shipley). Resist films of 30 to 70 nm thick were patterned with typical tip-sample voltages from –15 to –35 V, resulting in minimum feature sizes of 23 nm.¹¹⁶ Using self-assembled monolayers (SAMs) as resists (see also below), it was shown that the lower the exposure threshold energy of the film, the better the lithographic resolution. There are indications that, with these low voltages (~4 V), SAM resists will eventually yield sub-10 nm CDs. In an alternative approach, surface oxides were induced on Si and GaAs by slightly increased tip voltages on samples held in a wet nitrogen atmosphere.¹⁰² These thin oxides, although only a few monolayers thick, are sufficiently robust to act as a mask for subsequent reactive ion etching of the substrate.¹¹⁶ The oxidation process is fairly general and may also be applied to Ti and Cr. At NRL, oxide features with lateral dimensions as small as 10 nm have been achieved.¹¹⁶ Multilayer resist films for nanopatterning with SPL have also been developed. Sugimura et al. worked with a three-layer resist to pattern insulating substrates such as thermally grown SiO₂ with current injection from a scanning probe tip.¹¹⁹ The process sequence is sketched in Figure 1.46.

The bottom layer of the three-layer resist consists of 20 nm of amorphous Si (a-Si) and is prepared by ion-beam sputtering; a second layer consists of an intermediate 2 nm thick Si oxide and is prepared by photo-oxidation of the top layer of the amorphous Si. The top resist layer is 2 nm thick and consists of an octadecylsilyl self-assembled monolayer (ODS-SAM). To pattern the resist on top of the insulating SiO₂, a bias voltage is applied between the AFM probe and the conductive a-Si layer, which is biased positively. When a scanning probe is operated in the presence of atmospheric water vapor, the probe and sample are automatically connected via a minute water column created by capillary forces of the adsorbed water. This assembly serves as a minute electrochemical cell. As a result of the electrochemical anodization reaction, the monolayer resist becomes degraded in the region where the probe has passed, and the underlying photo oxide grows thicker. A subsequent etch in 0.5 wt.% HF removes the exposed oxide, and that pattern is then transferred to the underlying a-Si by an etch of the a-Si in an aqueous solution of 25 wt.% tetramethylammonium hydroxide

*Direct-Write
Technologies for
Rapid Prototyping
Applications*

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Direct-Write Technologies for Rapid Prototyping Applications: Sensors, Electronics, and Integrated Power Sources

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Technologies for Micrometer and Nanometer Pattern and Material Transfer

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1. INTRODUCTION

"Energy matters" is a flippant summary statement of Einstein's famous equation, $E = mc^2$. The assertion is correct in science, engineering and other human endeavors. The same is true of another terse statement, namely "size matters." There are many reasons for this: size can be an advantage or a disadvantage. It affects performance of people, animals, plants, and systems. Also, size certainly impacts the cost of manufactured objects. This chapter is concerned with making things on micrometer and smaller scales. It is useful to begin with a review of the scale against which objects are measured, as shown in Fig. 1.

One meter characterizes the familiar macroscopic scale in our world. In the recent decades, since the development of integrated circuits in the 1960s, the micrometer, or microscopic, scale has become quite well known. More recently, the regime between the macroscopic and microscopic arenas has been termed the mesoscopic. It includes old technologies, notably watch making, under a new moniker. In the 1990s, the scale appropriate to the size of atoms and molecules came to be called nanoscopic. Much of the work today in the fields of chemistry and materials science falls under this term.

Methods for the production and assembly of parts vary widely across these regimes, as indicated in Fig. 2. In the macro- and mesoscopic areas, parts are made individually and assembled piece-wise into products by companies in already very large industries. These size scales still involve much basic and applied research, but they are characterized by commercial engineering. The micrometer scale involves parallel production of objects, using pattern transfer and other methods, with layering or bonding being primary methods of assembly. The microelectronics industry, which took off in the 1960s, is already large, and the micromechanics industry began to grow exponentially in the 1990s. The micrometer arena still requires a great deal of basic and applied research. In the nanometer regime, a radically different approach to the production of objects is emerging; while the larger regimes have something of the character of sculpture, that is, being top-down approaches to making things, the bottom-up approach of chemistry and biology will dominate nanometer technology. Molecular synthesis and self-assembly are being envis-

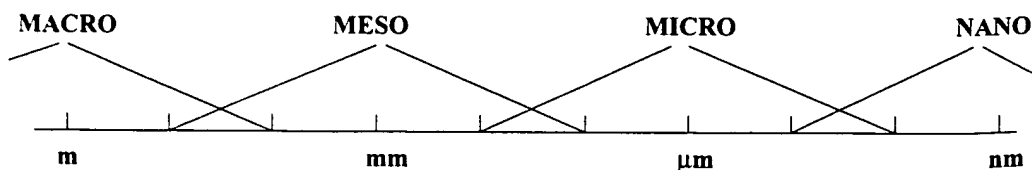


FIGURE 1 Size scale along which are shown the ranges of four major regimes of human-made objects.



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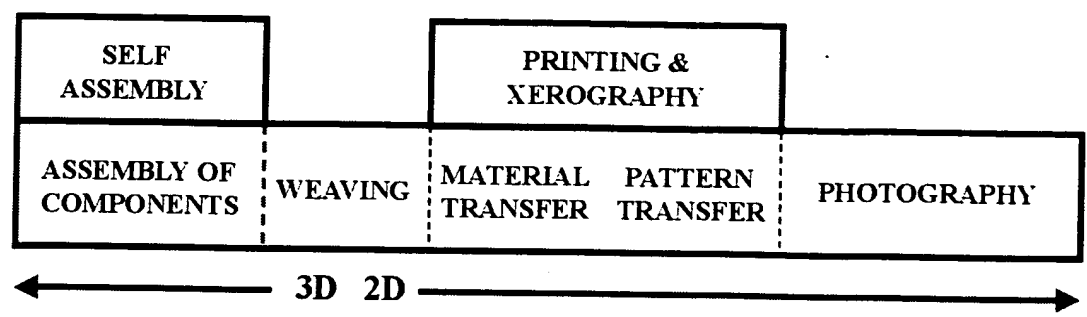


FIGURE 2 Relationships between the two (2D) and three (3D) dimensional ways to make and put parts together to make complex structures and devices, as well as two-dimensional patterns.

ioned as a primary approaches for making functional systems out of proteins and other organic materials on the nanometer scale. There are concepts for the production and use of molecular assembler devices, but they remain fraught with problems. Basic research still characterizes the state of what is called "nanotechnology." Some systems with components on the nanometer scale are already important commercially, but they have not reached the multibillion-dollar annual level that is the hallmark of industries on all the larger-size scales.

Devices and systems on the micrometer and smaller-size scales are decidedly three-dimensional. However, they are generally made by sequential use of thin-film technologies. Modern integrated circuits, for example, can have over 30 layers, which require over 200 process steps for their production. The three primary types of processes for production of familiar micrometer- and some new nanometer-scale devices are shown in Fig. 3. Pattern transfer, commonly called microlithography, is the movement of a design from an already-patterned

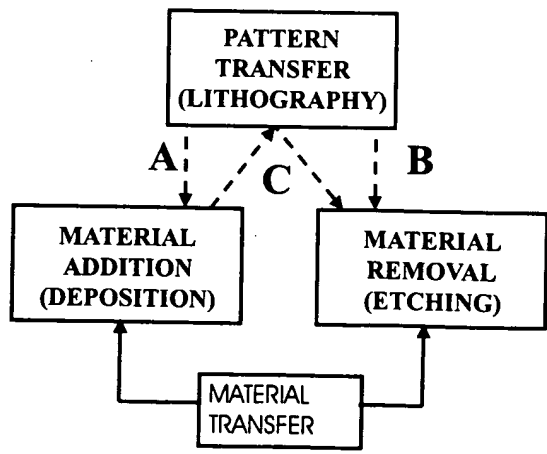


FIGURE 3 The dominant classes of processes used for manufacturing of micrometer-scale structures and devices. One class involves pattern transfer, with the other two being material transfer processes. The dashed lines indicate common process sequences, which are discussed in the text.